

Hexacoordinated Oligosilanes from a Hexacoordinated Silicon(IV) Complex Containing an O,N,N,O Salen-type and Thiocyanato-N Ligands

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Two new neutral hexacoordinated silicon complexes with SiN₄O₂ (**6**) and SiN₃O₂C (**7**) coordinating frameworks were synthesized by reaction of the O,N,N,O-donor salen-type ligand 1,2-bis[(2-hydroxy-4-methoxyphenyl)(phenyl)methylene]amino]ethane (H₂salen*) with Si(NCS)₄ and HMeSi(NCS)₂, respectively. The complexes **6** [Si(salen*)(NCS)₂] and **7** [Si(salen*)Me(NCS)] were studied in the solid-state by ²⁹Si and ¹⁵N CP/MAS NMR and in solution by ¹H, ¹³C, and ²⁹Si insensitive nuclei enhanced by polarization transfer (INEPT) NMR, UV/vis and FT-IR spectroscopy. Elemental analysis and single-crystal X-ray diffraction analysis were used to confirm the composition and structure for compounds **6** and **7**. Both complexes contain the dianionic salen-type ligand coordinated in an equatorial fashion to the silicon center, while the axial positions are occupied by two thiocyanato-N ligands for **6** and one thiocyanato-N and one methyl ligand for **7**. Complex **6**, which contains two Si–NCS functional groups, was used as monomer to produce a mixture of linear oligosilanes with a hexacoordinated silicon backbone (formulated SCN-[Si(salen*)]_n-NCS, *n* = 2–8) **8**, via a Wurtz-type coupling reaction. Oligomers **8** were identified by solid-state ²⁹Si cross polarization-magic angle spinning NMR and solution ¹H and ²⁹Si NMR spectroscopy, matrix assisted laser desorption ionization-time of flight (MALDI-TOF), gel-permeation chromatography (GPC), FT-IR, UV/vis spectroscopy and thermogravimetric analysis (TGA). Conclusive evidence of the oligomeric nature of **8** was provided by MALDI-TOF spectrometry and was supported by quantitative solution ²⁹Si NMR and GPC studies.

Introduction

The hypercoordinated silicon complexes containing salen-type ligands have received attention during the last ten years.^{1–11} The studies on this family of compounds have

been leading to new insights in the field of silicon coordination chemistry; for instance, in these compounds, unusual activation of Si–C⁵ and Si–Si⁶ bonds or intramolecular ligand charge transfer promoted by hexacoordinated silicon(IV) complexes has been observed.⁹ Some years ago, Roewer et al. demonstrated that the hexacoordinated silicon(IV) compounds **1** and **2** (Scheme 1), which contain a salen-type ligand and the SiCl₂ and SiF₂ functions, can undergo a Wurtz-type coupling reaction to produce the first examples of oligosilanes and polysilanes containing a hexacoordinated silicon backbone (**3**, Scheme 1).^{1,2}

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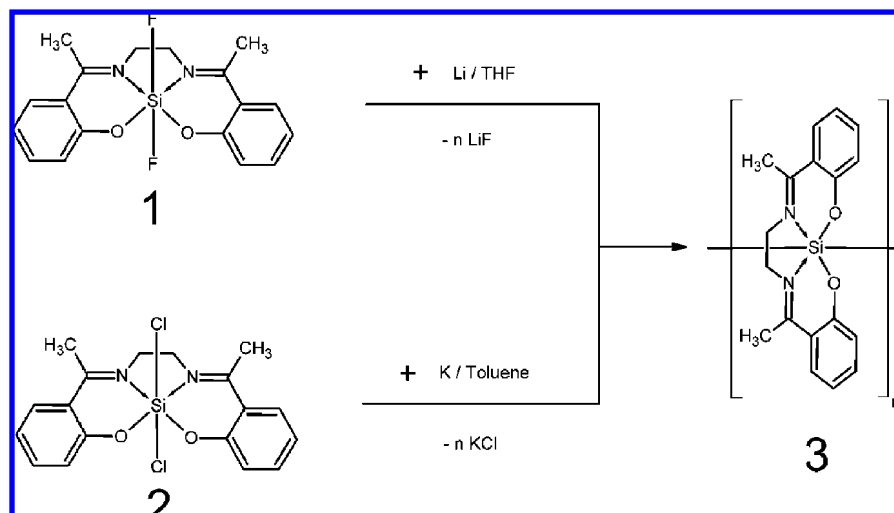
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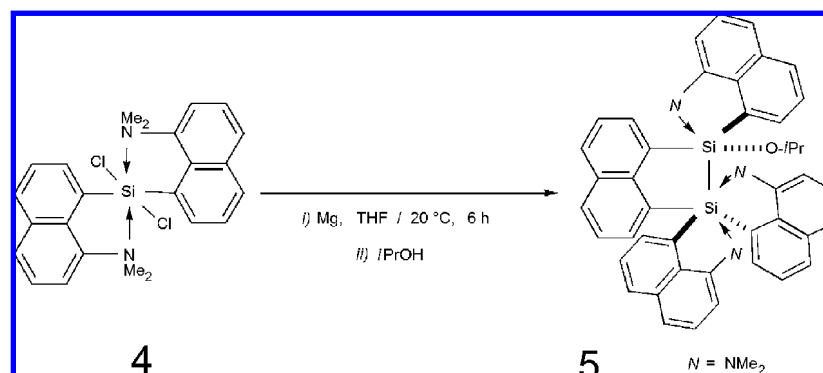
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Scheme 1



Scheme 2



Because of the unique well-known electronic and optical properties of tetracoordinated polysilanes which exhibit an extensive electron delocalization along the silicon backbone,¹² it has been proposed that the hypercoordinated polysilanes open new pathways in the design of nonlinear optics,¹³ photo-initiators,¹⁴ semiconductors,¹⁵ photo-conducting and liquid crystal materials.¹⁶ However, the polysilanes **3** obtained by Roewer et al. are poorly soluble in organic

solvents,¹ which prevent their study by techniques such as matrix assisted laser desorption ionization-time of flight (MALDI-TOF), gel-permeation chromatography (GPC), solution ²⁹Si NMR and UV/vis spectroscopies, which allow full characterization as well as to establish the properties of the new polysilanes. Tamao et al. attempted to polymerize the dichlorosilicon [4+2]-coordinated complex **4** containing 8-dimethylamino-1-naphthyl ligand but obtained disilane **5** which involved Si-Si and Si-C bond formation, as well as the amino group migration (Scheme 2).¹⁷

Tacke et al., by using $\text{Si}(\text{NCS})_4$ and $\text{Si}(\text{NCO})_4$ as sources of a silicon center, were able to prepare several examples of hypercoordinated silicon(IV) complexes containing the Si-NCO or Si-NCS functional groups, together with bidentate O,N- and tetradentate O,N,N,O-donor β -ketoenamines,¹⁸ bidentate O,O-donor β -diketone¹⁹ and tridentate O,N,O-chelating ligands.²⁰ The pseudohalogens NCO and NCS N-bonded to the silicon atom behave similarly to

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silicon-halogen function in substitution²¹ and condensation^{22,23} reactions, but, in addition, the reactions on the Si–NCX (X = O, S) bonds can occur with a higher selectivity than that observed for the Si–Cl bond.²³ In this regard, hypercoordinated silicon complexes containing one or two functional groups such as F, Cl, Br, NCO, and NCS may be considered potential sources for the preparation of Si–Si bonds by Wurtz-type coupling reactions, thus allowing the synthesis of disilanes, oligosilanes, and polysilanes containing a hypercoordinated silicon backbone. Recently, we reported the synthesis of new classes of highly coordinated silicon(IV) complexes by reacting methyl-di(thiocyanato-N)silane, HMeSi(NCS)₂ and HSi(NCS)₃ with tridentate N,N,O donor ligands that have OH and NH functional groups; we observed that the Si–H and Si–NCS bonds in HMeSi(NCS)₂ and HSi(NCS)₃ are easily replaced by Si–O and Si–N bonds through coordination with the organic ligand, maintaining one or two Si–NCS functionalities.²⁴

The studies reported here were carried out to establish that the Si–NCS functionalities in hexacoordinated silicon complexes can be used for the synthesis of oligo- or polysilanes with a hexacoordinated silicon backbone by means of a Wurtz-type coupling reaction with elimination of thiocyanate salts. The compounds Si(NCS)₄ and HMeSi(NCS)₂ were used as starting materials together with a salen-type ligand (H₂salen*) to obtain the new hexacoordinated silicon complexes **6** and **7**, which contain some remaining Si–NCS functional groups. In particular, we explored the synthetic potential of the neutral hexacoordinated silicon(IV) complex **6** which contains two Si–NCS functional groups, for the preparation of soluble oligosilanes with a hexacoordinated silicon backbone (**8**) via a Wurtz-type coupling reaction with metallic sodium in boiling toluene.²⁵ We considered that the solubility of the hypercoordinated silicon monomer and that of the oligosilanes and polysilanes that could be produced from the former, may be improved by inserting a CH₃–O fragment on the salen-type ligand.

Experimental Section

General Procedures. All reactions were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. The organic solvents were dried and purified according to standard procedures and stored under nitrogen. The ¹H and ¹³C solution NMR spectra were recorded at room temperature on a Varian Gemini 200 (200 MHz ¹H and 50 MHz ¹³C) spectrometer using CDCl₃. ¹H

and ¹³C NMR chemical shifts (δ) were determined relative to the residual CHCl₃ signals of the solvent (¹H, δ 7.26; ¹³C δ 77.0). Assignments of the ¹³C NMR data were supported by DEPT 135 experiments and ¹H, ¹H and ¹³C, ¹H correlation experiments. Solution ²⁹Si NMR and solid-state ²⁹Si and ¹⁵N cross polarization-magic angle spinning (CP/MAS) NMR spectra were recorded on a Varian Unity Plus 300 (²⁹Si 59.6 MHz and ¹⁵N 30.4 MHz) or a Bruker Avance 400 (²⁹Si 79.5 MHz) spectrometer (Bruker Analytik GmbH Karlsruhe, Germany) equipped with a Bruker Ultrashield 9.4 T, 8.9 cm vertical-bore superconducting magnet. Chemical shifts (δ) were determined relative to external standard TMS (solution ²⁹Si, δ 0.0, ²⁹Si CP/MAS, δ 0.0) and NH₄NO₃ (¹⁵N CP/MAS δ 0.0). The ²⁹Si CP/MAS NMR spectra were recorded at room temperature (20°C) with 4 ms CP contact time, 4 s recycle delay, 41000 averages, and 80 Hz line broadening. Representative samples were ground and packed in 4 mm zirconia's rotors, sealed with Kel-F caps, and spun at 5 kHz. The 90° pulse width was 3.5–4.5 μs, and high power proton decoupling was used. UV/vis spectra were recorded on an Agilent 8435 UV/vis Spectrometer; all UV/vis spectra were obtained in quartz cuvettes of 1.0 cm width. FT-IR spectra were recorded on a Spectrum 100 FT-IR Perkin Elmer spectrometer and melting points were determined in sealed capillaries and are not corrected. MALDI-TOF spectra were recorded on a Voyager DE-PRO time-of-flight mass spectrometer (Applied Biosystems) equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse width and working in positive ion mode and delayed extraction; a high acceleration voltage of 25 kV was employed. Dithranol [1,8-dihydroxyanthracen-9(10H)-one] at a concentration of 10 mg/mL in acetonitrile was used as matrix. Samples were dissolved in acetonitrile and mixed with the matrix at a molar ratio of approximately 1:100. The average molecular weight (*M_w*) and polydispersity index (*M_w*/*M_n*) of the oligomers of **8** were measured relative to polystyrene standards (1100–3000 Da) on a Perkin Elmer Series 200 system equipped with three 5 mm PL-gel columns with pore size of 10³, 10⁴, and 10⁵ Å, and a Series 200 refractive index detector in tetrahydrofuran solution. The degree of polymerization of **8** was calculated on the basis of the MALDI-TOF analysis, GPC and quantitative solution ²⁹Si NMR spectroscopy. The thermogravimetric analysis was carried out under nitrogen atmosphere on a TA Instruments TGA Q500. Elemental analyses were performed with a Thermo-Finnigan Flash 1112 instrument at the Chemistry Department of the Cinvestav (Mexico City). Photo-irradiation was done in quartz cuvettes of 1.0 cm width at 25 °C using a Camag (Muttenz-Switzerland) Universal UV Lamp 29100 at λ = 366 nm. During photo-irradiation, samples were constantly mixed using a magnetic stirrer.

The starting materials HMeSi(NCS)₂^{24a} and Si(NCS)₄,²⁶ and the O,N,N,O donor 1,2-bis[[2-hydroxy-4-methoxyphenyl](phenyl)methylene]amino]ethane ligand (H₂salen*)²⁷ were prepared as reported in the literature.

Synthesis of [Si(salen*)(NCS)₂] **6.** The ligand H₂salen*, 1,2-Bis[[2-hydroxy-4-methoxyphenyl](phenyl)methylene]amino]ethane, (1.22 g, 2.52 mmol) was added to the stirred suspension of Si(NCS)₄ (0.65 g, 2.50 mmol) in acetonitrile (20 mL). After stirring for 24 h at room temperature, 60 mL of acetonitrile were added to the reaction mixture which was then heated to 80 °C, filtered off and discarding any undissolved material. The clear solution was slowly cooled to –20 °C and left overnight, forming yellowish crystals that were separated by filtration, washed with diethyl ether

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(20 mL), and dried under vacuum (0.01 mbar) for 2 h. The mother liquors were concentrated to 40 mL and then stored at $-20\text{ }^{\circ}\text{C}$ for 12 h, thus allowing for crystallization of an additional quantity of compound **6**, which was treated in the same way as in the first crystallization. Overall yield 68.0 % (1.06 g, 1.70 mmol). Compound **6** did not melt below $270\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_2\text{Si}$ (622.78 g mol^{-1}): C, 61.71; H, 4.21; N, 9.00; S, 10.30. Found: C, 61.97; H, 4.27; N, 8.94; S, 12.50. ^1H NMR (200 MHz, CDCl_3): δ 3.59 (s, 4H, CH_2), δ 3.88 (s, 6H, OCH_3), δ : 6.30–6.36 [dd, $^3J(\text{H},\text{H})$ 11.6 Hz, $^4J(\text{H},\text{H})$ 2.5 Hz, 2H, CH aromatic], δ : 6.63–6.64 [d, $^3J(\text{H},\text{H})$ 2.4 Hz, 2H, CH aromatic], δ : 6.67–6.72 [d, $^3J(\text{H},\text{H})$ = 9.1 Hz, 2H, CH aromatic], δ : 7.32–7.37 (m, 4H, CH aromatic), δ : 7.53–7.56 (m, 6H, CH aromatic). ^{13}C NMR (50 MHz, CDCl_3): δ 47.9 (CH_2), δ 55.7 (OCH_3), δ : 104.0, 109.6, 126.7, 129.2, 130.0, 135.0 (CH aromatic); NCS was not detected. ^{29}Si INEPT NMR (59.6 MHz, CDCl_3) δ -207.0 . ^{29}Si NMR CP/MAS (59.6 MHz) δ -199.0 . ^{15}N CP/MAS NMR (30.5 MHz): δ : -165.8 , -174.6 ($\text{N}=\text{C}$), δ : -222.5 , -227.4 (NCS). FT-IR (KBr): $\nu(\text{NCS})$ 2083.0 cm^{-1} , $\nu(\text{N}=\text{C})$ 1532.0 cm^{-1} .

Synthesis of [Si(salen*)Me(NCS)] 7. The ligand H_2salen^* , 1,2-bis[[[2-hydroxy-4-methoxyphenyl](phenyl)methylene]amino]ethane, (3.95 g, 8.22 mmol) was added to the stirred solution of $\text{HMeSi}(\text{NCS})_2$ (1.12 g, 7.01 mmol) in acetonitrile (20 mL). The reaction mixture was stirred for 24 h at room temperature producing a pale yellow solid that was dissolved by heating the solution to $80\text{ }^{\circ}\text{C}$ and then it was slowly cooled down to $20\text{ }^{\circ}\text{C}$. The pale yellow crystals that formed were removed by filtration, washed with 20 mL diethyl ether, and dried under vacuum (0.01 mbar) for 3 h. Yield 2.1 g (50.8 %). Mp: $230\text{ }^{\circ}\text{C}$ (dec). Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{N}_3\text{O}_4\text{SSi}$ (579.74 g mol^{-1}): C, 66.30; H, 5.04; N, 7.25; S, 5.53. Found: C, 65.83; H, 4.99; N, 7.14; S, 5.34. ^1H NMR (200 MHz, CDCl_3): δ 0.36 (s, 3H, SiCH_3), δ 3.53 (s, 4H, CH_2), δ 3.84 (s, 6H, OCH_3), δ 6.23 [dd, $^3J(\text{H},\text{H})$ 11.6 Hz, $^4J(\text{H},\text{H})$ 2.5 Hz, 2H, CH aromatic], δ : 6.56–6.57 [d, $^3J(\text{H},\text{H})$ 2.5 Hz, 2H, CH aromatic], δ : 6.61–6.66 [d, $^3J(\text{H},\text{H})$ 9.0 Hz, 2H, CH aromatic], δ : 7.38–7.58 (m, 8H, CH aromatic). ^{13}C NMR (50 MHz, CDCl_3): δ 10.7 (SiCH_3), δ 48.0 (CH_2), δ 55.5 (OCH_3), δ : 103.9, 108.2, 126.0, 127.2, 128.9, 129.2, 129.6, 134.7 CH aromatic, δ 131.8 (NCS). ^{29}Si INEPT NMR (59.6 MHz, CDCl_3): δ -170.8 . ^{29}Si CP/MAS NMR (59.6 MHz): δ -172.6 . ^{15}N CP/MAS NMR (30.4 MHz): δ -210.2 (NCS), δ : -155.8 , -159.4 ($\text{N}=\text{C}$). FT-IR (KBr): $\nu(\text{NCS})$ 2084.0 cm^{-1} , $\nu(\text{N}=\text{C})$ 1585.0 cm^{-1} .

Synthesis of $\text{SCN}[\text{Si}(\text{salen}^*)]_n\text{NCS}$ ($n = 2\text{--}8$) 8. Metallic sodium (0.25 g, 10.80 mmol) was added to the magnetically stirred suspension of complex **6** (1.56 g, 2.51 mmol) containing some glass balls (2 to 3 mm diameter) in 10 mL of toluene. The reaction mixture was refluxed for 24 h and then kept undisturbed at $20\text{ }^{\circ}\text{C}$ overnight. The solid that formed (NaNCS and unreacted sodium) was filtered off and discarded, and the filtrate was carefully layered with diethyl ether (20 mL) and kept undisturbed at $-10\text{ }^{\circ}\text{C}$ overnight, producing a pale orange precipitate of **8** that was removed by filtration and washed subsequently with diethyl ether (2×20 mL), hexanes (2×20 mL) and dried under vacuum (0.01 mbar) for 8 h. Yield 52.4 % (0.70 g, 0.33 mmol).²⁸ Product **8** is soluble in solvents such as chloroform, dichloromethane, tetrahydrofuran, and acetone, giving in all cases red-colored solutions. The mixture of oligomers **8** was analyzed by MALDI-TOF, GPC, and TGA. ^1H NMR (200 MHz, CDCl_3): δ 3.81 (s, CH_2), δ 3.70 (s, OCH_3), δ : 6.3–7.5 (m, CH aromatic) where all signals were broad. ^{29}Si CP/MAS NMR (79.5 MHz): δ -126.9 (broad). ^{29}Si NMR (59.6 MHz, CDCl_3): δ -126.6 (silicon backbone), δ -127.8 (terminal

silicon). FT-IR (KBr): $\nu(\text{NCS})$ 2060.0 cm^{-1} , $\nu(\text{N}=\text{C})$: 1606.0 , 1591.0 cm^{-1} .

Crystallographic Structure Determinations. Suitable single-crystals of **6** and **7** were obtained by slowly cooling their solutions in CH_3CN from $80\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$ in about 12 h by keeping the flasks with the solutions inside a Dewar flask. The crystals were coated with dry perfluoropolyether and were mounted on a glass fiber under a cold nitrogen stream [$100(2)\text{ K}$]. Intensity data were collected on a Bruker-Nonius X8Apex-II CCD diffractometer equipped with a Mo $\text{K}\alpha_1$ radiation ($\lambda = 0.71073\text{ \AA}$) source and graphite monochromator. All structures were solved by direct methods with SIR 2004²⁹ and refined by full-matrix least-squares procedures utilizing SHELXL-97.³⁰

Results and Discussion

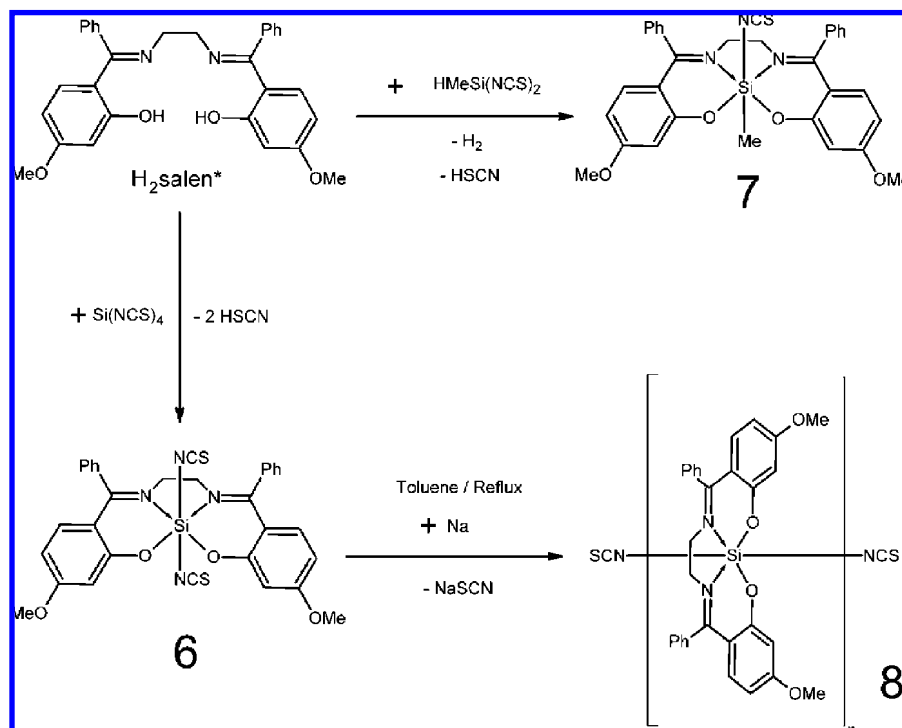
Treatment of the salen-type ligand (H_2salen^*) with $\text{Si}(\text{NCS})_4$ or $\text{HMeSi}(\text{NCS})_2$ produces compounds **6** [$\text{Si}(\text{salen}^*)(\text{NCS})_2$] and **7** [$\text{Si}(\text{salen}^*)\text{Me}(\text{NCS})$] at 68 and 51 % yield, respectively (Scheme 3). The complexes precipitate from acetonitrile, giving pale yellow solids. The solids formed are recrystallized by slow cooling in acetonitrile to give suitable crystals for X-ray diffraction analyses that confirm the structures of **6** and **7**; these compounds maintain, in the coordination sphere, two and one NCS functional groups, respectively.

^{29}Si NMR chemical shifts in the solid-state and in solution for complex **6** are consistent with a SiO_2N_4 hexacoordinated complex,¹⁸ while in the case of **7** those values correspond to a $\text{SiO}_2\text{N}_3\text{C}$ hexacoordinated complex.³¹ The solution ^1H and ^{13}C NMR data in CDCl_3 for compounds **6** and **7** indicate the presence of one single isomer for each complex, showing one set of resonance signals for the O,N,N,O-salen-type ligand (H_2salen^*) which are consistent with the X-ray crystal structures observed in the solid-state. Nevertheless, complex **6** exhibited different ^{29}Si NMR chemical shifts in the solid state (-207.0 ppm) and in solution (-199.0 ppm), which suggested that an isomerization process occurred in CDCl_3 solution, probably between *trans* and *cis* isomers; however, the isomerization was not detected on the ^1H NMR time scale. The ^{13}C NMR and DEPT 135 spectra for the hexacoordinated monoorganosilane **7** with a $\text{SiO}_2\text{N}_3\text{C}$ skeleton showed one independent signal for each of the *ortho*- and *meta*-hydrogens of the phenyl group attached to the imine carbon, which indicated the existence of a barrier to rotation. Similar behavior has been observed for other silicon complexes obtained with the same H_2salen^* ligand used in this work.⁵ In contrast, the phenyl rings on the hexacoordinated complex **6** with the totally inorganic SiO_4N_2 coordination framework are free to rotate.

Complex **6** crystallized in the $P21/c$ space group with two independent molecules in the asymmetric unit, while **7** crystallized in the Cc space group with one molecule in the asymmetric unit. The Si coordination polyhedron in both cases corresponds to a distorted octahedron; the structures of molecules **6** and **7** are depicted in Figures 1 and 2. Both complexes contain the salen-type ligand coordinated in an equatorial fashion, and the axial positions are occupied by the two thiocyanato-N ligands in the case of **6** and by the thiocyanato-N ligand and the methyl ligand in the case of **7**.

(28) Yield was calculated considering that **8** corresponds, on the average, to tetrasilane $\text{SCN}[\text{Si}(\text{salen}^*)]_4\text{NCS}$.

Scheme 3



The crystal data and the experimental parameters used for the crystal structure analyses of **6** and **7** are summarized in Table 1.

Crystallographic structural differences between the two independent molecules in the asymmetric unit of **6** are minimal and thus, in the discussion that follows, only the data of one of the conformers will be considered. In both complexes **6** and **7**, the ligand coordinated in an equatorial

fashion has the four donor atoms of the coordination framework (SiO_2N_2) practically in the same plane (the sum of the angles $O1-Si1-N1$, $N1-Si1-N2$, $O1-Si1-O2$, and $O2-Si1-N2$ equals 360° for **6** and 358.54° for **7**), but the overall framework of the ligand is nonplanar for the two complexes.

The $Si-NCS$ bond distance in **7** ($Si1-N3$) is significantly longer than the two $Si-NCS$ bond distances for **6** ($Si1-N3$ and $Si1-N4$), while the $Si-CH_3$ bond distance in **7** ($Si1-C31$) is slightly shorter than that reported for analogous hexacoordinated diorganosilicon compounds.^{7,8} Thus, the presence of the methyl ligand instead of a $-NCS$ ligand in complex **7** causes elongation of the trans $Si-NCS$ bond length. The $Si-NCS$ lengths in **6** are in the range of the

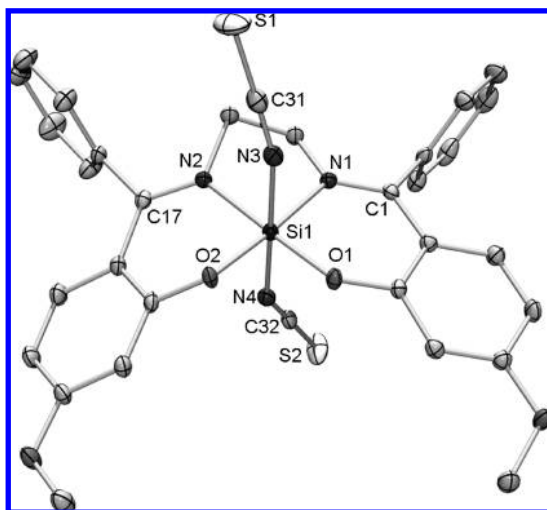


Figure 1. ORTEP view of compound **6** drawn at the 50% probability level. The crystallographic asymmetric unit presents two symmetrically independent molecules of the same structure. Only one independent molecule is shown. The hydrogen atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [deg]: $Si1-N1$ 1.9063(14), $Si1-N2$ 1.9133(15), $Si1-O1$ 1.7029(12), $Si1-O2$ 1.7137(12), $Si1-N3$ 1.8482(16), $Si1-N4$ 1.8679(15), $N(1)-C(1)$ 1.308(2), $N(2)-C(17)$ 1.305(2); $N3-Si1-N4$ 174.19(7); $O1-Si1-N2$ 178.37(6); $O2-Si1-N1$ 175.46(6); $N1-Si1-N2$ 84.02(6); $O1-Si1-O2$ 90.16(6); $O1-Si1-N1$ 94.36(6); $O2-Si1-N2$ 91.46(6), $N3-C31-S1$ 178.67(18), $N4-C32-S2$ 179.10(18), $C31-N3-Si1$, 160.52(15), $C32-N4-Si1$ 149.31(14).

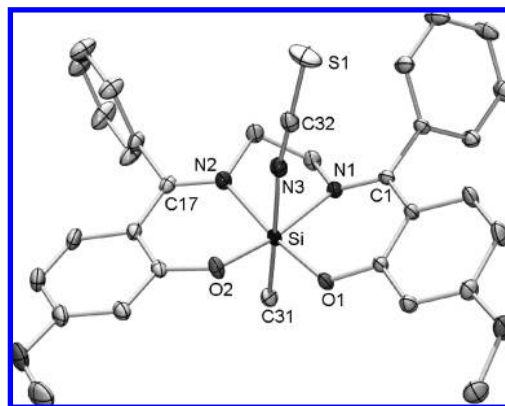


Figure 2. ORTEP view of compound **7** drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [deg]: $Si-N1$ 1.9233(10), $Si-N2$ 1.9455(11), $Si-N3$ 1.9613(11), $Si-O1$ 1.7258(9), $Si-O2$ 1.7371(9), $Si-C31$ 1.9016(13), $N1-C1$ 1.3024(15), $N2-C17$ 1.2998(16); $C31-Si-N3$ 175.84(5), $O1-Si-N2$ 172.43(5), $O2-Si-N1$ 167.37(5), $N1-Si-N2$ 83.77(4), $O1-Si-O2$ 89.53(4), $O1-Si-N1$ 92.15(4), $O2-Si-N2$ 93.09(4), $N3-C32-S1$ 179.57(13), $C32-N3-Si$ 169.34(10).

Table 1. Summary of Crystallographic Data and Structure Refinement Results for **6** and **7**

	6	7
formula	C ₃₂ H ₂₆ N ₄ O ₄ S ₂ Si	C ₃₂ H ₂₉ N ₃ O ₄ SSi
formula mass, g mol ⁻¹	622.78	579.73
collection <i>T</i> , K	100(2)	100(2)
λ (Mo K α), Å	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	P2 ₁ /c	Cc
<i>a</i> , Å	11.2201(5)	9.8810(4)
<i>b</i> , Å	15.3980(7)	17.1466(7)
<i>c</i> , Å	34.5168(16)	17.3434(8)
α , deg	90	90
β , deg	91.786(3)	93.194(2)
γ , deg	90	90
<i>V</i> , Å ³	5960.5(5)	2933.9(2)
<i>Z</i>	8	4
ρ (calcd), Mg m ⁻³	1.388	1.312
<i>F</i> (000)	2592	1216
crystal dimensions, mm	0.31 × 0.19 × 0.18	0.50 × 0.28 × 0.26
θ range, deg	1.45–30.58	2.38–30.58
no. of collected reflections	97001	40915
no. of independent reflections/parameters	18056/779	7704/373
<i>R</i> _{int}	0.0660	0.0252
<i>R</i> ₁ (<i>F</i>) [<i>F</i> ² >2 σ (<i>F</i> ²)] ^a	0.0481	0.0279
<i>wR</i> ₂ (<i>F</i> ²) ^b (all data)	0.1104	0.0694
<i>S</i> ^c (all data)	1.012	1.040
max./min. residual electron density, e Å ⁻³	+0.485/−0.545	+0.290/−0.293

^a $R_1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for the observed reflections [$F^2 > 2\sigma(F^2)$].
^b $wR_2(F^2) = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum w(F_o^2)^2 \}^{1/2}$. ^c $S = \{ \sum [w(F_o^2 - F_c^2)]^2 / (n - p) \}^{1/2}$; (*n* = number of reflections, *p* = number of parameters).

bi-functional NCS hexacoordinated silicon(IV) complexes previously reported (1.8482–1.8679 Å)^{18,19a,24a} and, as expected, they are significantly longer than a bifunctional -NCS pentacoordinate silicon(IV) complex.²⁰ On the other hand, one of the Si–N–CS angles in **6** (C31–N3–Si1, 160.5°) is smaller than that observed for **7** (C32–N3–Si1 169.3°), but the second Si–N–CS angle in **7** is even smaller (C32–N4–Si1 149.3°). These observations point out that a *trans* effect among the axial ligands is present in complexes **6** and **7**. In both complexes, the N–C–S angles of the thiocyanato-N ligands are quite similar, near 180°.

Complex **6** was used as starting material for the preparation of oligosilanes **8** via Wurtz-type coupling reaction with metallic sodium in boiling toluene (Scheme 3). The pale orange-reddish microcrystalline powder **8** can be formulated as SCN-[Si(salen*)]_{*n*}-NCS, which is air stable for several days, as well as its precursor **6**. The ²⁹Si CP/MAS NMR spectrum of the mixture of oligosilanes **8** shows a broad signal at −127.0 ppm; this is consistent with Si centers in a Si_{*n*} and SiO₂N₂ skeleton perpendicular to the chain;^{1,2} the signal at −127.0 ppm shows a shoulder at higher field that can be assigned to the (salen*)Si–NCS end groups. The quantitative ²⁹Si NMR spectrum in CDCl₃ solution displayed two signals at −126.6 and −127.8 ppm at an approximately 1:1 ratio, corresponding to the silicon backbone and to the terminal silicon atoms, respectively. These NMR data suggest that, in solution, **8** exists mainly as a tetrasilane (*M*_W = 2142, degree of polymerization *Dp* = 4). However, a multimodal distribution is observed by GPC, where the values obtained were: *M*_n = 738, *M*_W = 1223, *Dp* = 2 and *M*_W/*M*_n = 1.66. The differences of the weight-average molar mass *M*_W and of the degree of polymerization *Dp* obtained by quantitative

²⁹Si NMR with respect to those values obtained by GPC measurements can be attributed to the difference in hydrodynamic volume between the polystyrene standard and the oligosilanes in the GPC experiment.

The MALDI-TOF spectrum gives conclusive data regarding the nature of the mixture of oligosilanes **8** (Figure 3A), showing a concatenation of up to eight silicon atoms (*n* = 8, *Dp* = 8), and two types of signals can be distinguished in the spectrum (Figure 3B): one due to the neutral oligomer species with a hydroxyl end group (a) and another from cationic oligomers with a dithranol and thiocyanato-N or hydroxyl end groups (b); both species may be formed during the MALDI sample preparation. In Figure 3B, an expansion of the zone between 900 and 1600 Da is shown. This region corresponds to the mass peak pattern for the disilanes (*n* = 2) and trisilanes (*n* = 3), where peaks at *m/z* = 1046.9 and *m/z* = 1553.0 correspond to neutral disilane and trisilane, respectively. The most intense peaks, *m/z* = 1032.3 and 1538.6, are due to disilanes and trisilanes without a methyl fragment and with two hydroxyl end groups (a). The difference of mass between *n* = 3 and *n* = 2 is 506 Da, which corresponds to the repeating unit of the oligosilanes: the silicon atom bonded to the polydentate ligand, Si(salen*). The peak at *m/z* = 1267.4 corresponds to the monocationic disilane without two methyl fragments and with dithranol and thiocyanato-N fragments as end groups (b), while the peak at *m/z* = 1213.0 is due to the dicationic disilane without three methyl fragments and with dithranol and hydroxyl fragments as end groups (b).

The thermal degradation of **8** was monitored with a thermogravimetric analyzer (TGA). Samples were heated from ambient temperature to 800 °C at a heating rate of 5 °C/min. At 225 °C, a weight loss of 9.5 % is observed, and this can be attributed to the loss of methoxy fragments on the ligand. The highest weight loss (45.8%) occurred between 225 and 780 °C, which may correspond to the decomposition of the remainder of the organic ligand; the losses that follow may correspond to the formation of residual silicon carbide.²

Some information about the electronic behavior of compounds **6**, **7**, and **8** was obtained by means of UV/vis spectroscopic studies. Figure 4A shows comparative UV/vis spectra of the monomer **6** and the oligosilanes **8** in chloroform solution. The UV/vis spectrum of **6** shows two intense absorptions at λ_{\max} 312 nm (ϵ 21122 L mol⁻¹ cm⁻¹) and λ 351 nm (ϵ 13591 L mol⁻¹ cm⁻¹), while the absorption bands of the oligosilanes **8** appear at λ_{\max} 291 nm (ϵ 33734 L mol⁻¹ cm⁻¹) and λ 338 nm (ϵ 16432 L mol⁻¹ cm⁻¹),³² blue-shifted with respect to monomer **6**. The extinction coefficients in these spectra are out of range with respect to those observed for typical tetravalent polysilanes (5000 to 10000 L mol⁻¹ cm⁻¹),^{12a} suggesting that these absorptions

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(32) The extinction coefficients (ϵ) were calculated on the base of disilane (*n* = 2) species; for tetrasilane (*n* = 4) the values are λ_{\max} 291 nm, ϵ 64000 L mol⁻¹ cm⁻¹ and λ 338 nm, ϵ 35200 L mol⁻¹ cm⁻¹.

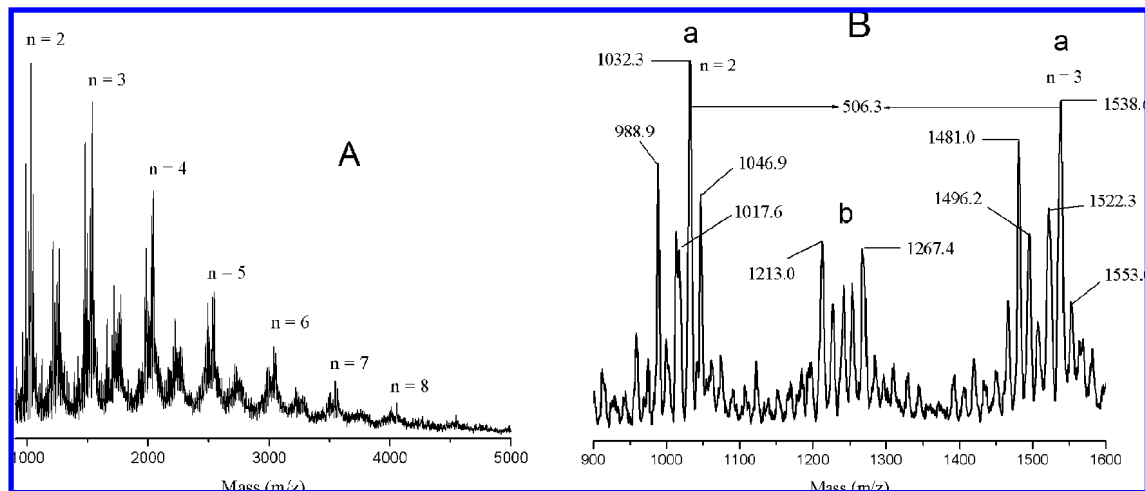


Figure 3. (A) MALDI-TOF spectrum of the oligosilanes **8**. (B) Expanded view for 900–1600 Da showing the peak pattern fragments for disilane $n = 2$, m/z 1046.9 and trisilane $n = 3$, m/z 1553.0.

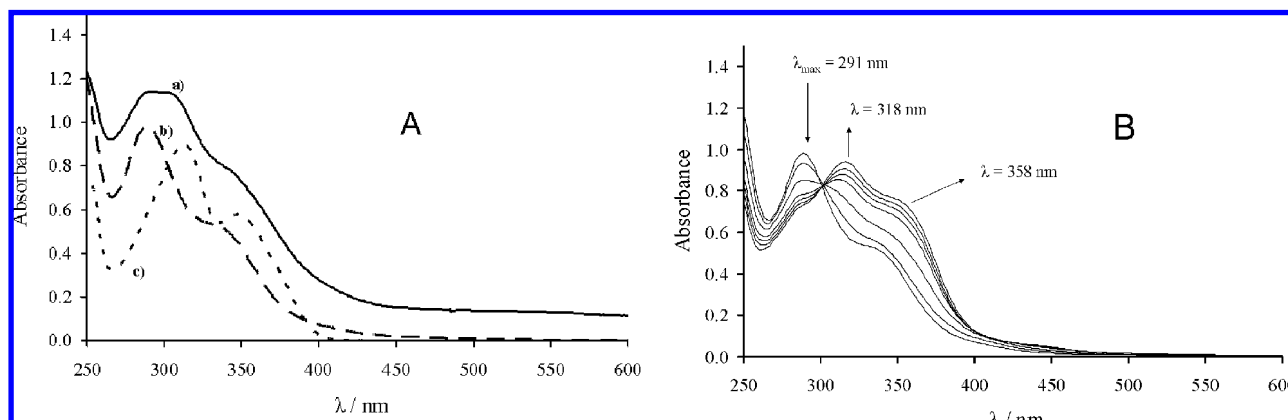


Figure 4. (A) UV/vis spectra of (a) **8** in solid film, (b) **8** in chloroform solution (0.028 mmolar), and (c) **6** in chloroform solution (0.038 mmolar). (B) UV/vis spectra of **8** after photo-irradiation every 30 s with UV/vis λ 366 nm. Isosbestic point is at λ 303 nm.

are due to conjugation in the salen-type ligand. However, absorptions could be affected by the different conformations adopted by oligomers **8**—it is well-known that the electronic properties of polysilanes are affected by polymer conformation, degree of polymerization, substituents attached to the polymer chain,³³ and by coordination number.³⁴ Interestingly, oligosilanes containing pentacoordinate silicon moieties in a trisilane backbone can reduce excitation energies of the Si–Si bond.^{34a,b} In contrast, the incorporation of two pentacoordinate silicon atoms in a tetrasilane backbone increases the excitation energies of the Si–Si bond; this electronic behavior was attributed to a conformational effect on the electronic structure.^{34c,d}

The UV/vis spectra of the oligosilanes **8** in solid film and in chloroform solution are almost identical, thus suggesting that they maintain the same conformation both in solution and in the solid state.³⁵ The UV/vis spectrum of **7** is quite similar to that of **6** and shows the absorption bands at λ_{\max} 315 nm (ϵ 27829 L mol⁻¹ cm⁻¹) and λ 360 nm (ϵ 15207 L mol⁻¹ cm⁻¹), and a new band appears at λ 283 nm (ϵ 21235 L mol⁻¹ cm⁻¹), which may be attributed to the σ – σ^* transition band of the Si–C bond.

The oligomers **8** displayed changes after irradiation by UV/vis light at 366 nm in CHCl₃ solution. The band at λ_{\max} 291 nm tends to disappear, and a new absorption band at λ 318 nm appears, while the band at λ 338 nm (shoulder) is red-shifted and an isosbestic point is observed at 303 nm for this process (see Figure 4b). However, no change is observed in polar solvents such as acetonitrile, THF, or in solid film after 20 min of UV irradiation. The change in absorbance could be due to Si–Si bond cleavage; however, the typical photochemical bleaching pattern of tetravalent polysilanes^{12a} was not observed. This suggests that this behavior is due to a conformational rearrangement of the oligosilanes.

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Further studies are necessary to obtain more information on the conformation of the oligosilanes **8** mixture and the susceptibility of the Si–Si bond to cleavage upon irradiation by UV/vis light. We are currently studying the synthesis of polysilanes with higher molecular weights.

Concluding Remarks

The complex **6** [Si(salen*)(NCS)₂] can undergo Si–Si coupling reactions to give linear oligosilanes containing a hexacoordinated silicon backbone (**8**). MALDI-TOF along with the quantitative ²⁹Si NMR and GPC analyses showed that **8** is best described as a mixture of di-, tri-, tetra-, and oligosilanes with a hexacoordinate silicon backbone of up to eight concatenated silicon atoms: SCN-[Si(salen*)]_n-NCS (*n* = 2–8). These results clearly demonstrate the synthetic potential of hypercoordinated silicon complexes with the Si–NCS function for the preparation of hypercoordinated Si–Si bonds. Moreover, starting materials of the type Si(NCS)₄ and HMeSi(NCS)₂ react by way of Si–NCS and Si–H moieties with OH and NH functional groups of ligands

such as salen-type molecules²⁴ to give cleanly neutral hypercoordinated silicon complexes without requiring the addition of triethylamine, which is normally employed when chlorosilanes are used as starting materials, with the added complication of by-product removal.

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Supporting Information Available: Representative GPC chromatograph, solid-state and solution (CDCl₃) ²⁹Si NMR spectra of **8**, and data from X-ray crystallographic analysis of the compounds **6** and **7** in crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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